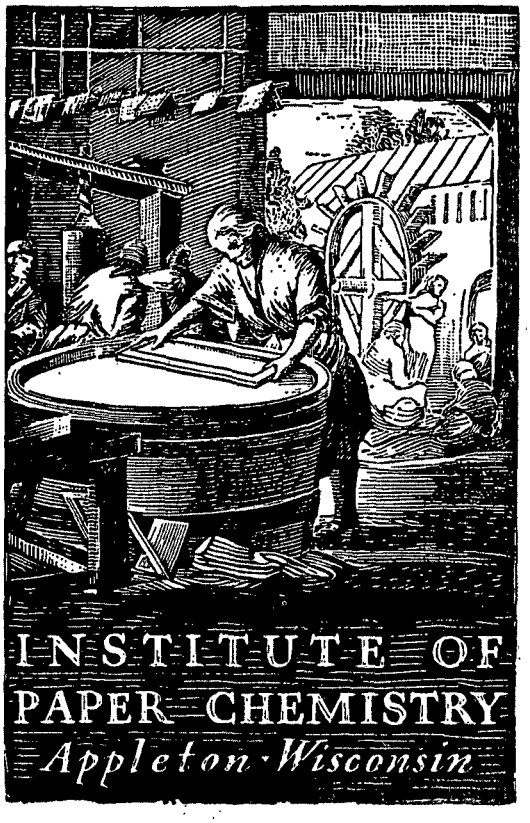

THE EFFECTS OF RECYCLED WHITE WATER ON PERFORMANCE OF POLYMER RETENTION AND DRAINAGE AIDS

Project 3276

Report Four

MILL TRIAL OF ENZYME TREATMENT OF BROKE

A Progress Report

to

MEMBERS OF PROJECT 3276

March 1, 1979

THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

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THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

MILL TRIAL OF ENZYME TREATMENT OF BROKE

SUMMARY

A long-standing problem in paper manufacture is the interference of starch with filled furnishes. Low filler retention, poor saveall efficiency, and difficulties in removal of suspended solids in the primary clarifier are characteristic of the problem.

A possible solution is to degrade the starch with a suitable enzyme, alpha-amylase. The resulting starch fragments are not able to coat the filler particles and to thereby produce retention and flocculation problems. Although enzyme treatments are mentioned in the literature, it was believed that further work should be done to characterize the potential of this method.

Initial laboratory studies defined the optimum conditions for use of the enzyme. A low dosage of enzyme, when used at a pH near neutrality, provided greatly improved filler retention. Benefits remained constant within a temperature range of 70 to 185°F. However, higher temperatures prevailing in the paper driers denatured the enzyme, and no enzyme activity remained in the thermally dried sheets.

The second phase of the study involved mill trials of the enzyme treatment on a machine running a fine grade of paper. The paper being produced contained about 9% ash, one-third of which was titanium dioxide. Starch was added to the paper only at the size press. Some of this starch, however, eventually entered the wet end of the paper machine by way of the repulped broke. During a portion of the trial the starch-specific enzyme was added to the broke in the hydrapulper, where the pH and reaction time could be controlled.

Samples of paper and stock from various wet end locations were collected during both treatment and nontreatment periods throughout the 24-hour trial. Enzymatic degradation of starch increased first pass filler retention to 65% from a level of 40%. Suspended solids concentration in the clear leg of the save-all dropped 86%, indicating substantially improved efficiency in this unit. In addition, polymer retention aid dosage could be cut 80% from the normal level while maintaining specifications for brightness and opacity.

Economic analyses showed a net saving from enzyme treatment, primarily as a result of less titanium dioxide loss to the sewer. Fewer wet end upsets and a more uniform product would be anticipated in long-term use of the treatment.

Based upon the results of this study, it appears that enzymatic degradation of starch could have many beneficial applications in the paper industry to alleviate problems with filler retention and suspended solids removal caused by starch.

INTRODUCTION

Starch and its derivatives are some of the most useful additives in papermaking. As adhesives, binders for coatings, and surface sizing agents they find broad application in the paper and board industry. This is due to both their effectiveness and especially their relatively low cost.

However, starch in the wet end has long been known to cause reduced filler retention. In 1935 Willets (1) discussed the problem and suggested that the starch adsorbed on the filler particles to form a "protective colloid" about them. The particles are thus prevented from being flocculated or retained by a large free energy (entropic) barrier. In the drug, paint, and other industries this kind of dispersing effect is put to good use. Several theories have been advanced to describe the effect, currently known as "steric stabilization." A recent review (2) outlines our present understanding.

The severity of the problem in papermaking depends upon the type of starch (3), with hypochlorite-oxidized starch being acknowledged (1,3,4) as the most detrimental to filler retention. It has been suggested (5) that the latter, in addition to causing steric stabilization, carries a strongly negative charge and further enhances dispersion by charge repulsion of its ionized carboxyl groups. Cationic starches, so long as overdosing is avoided, do not decrease retention (3,6). In fact they are often used as retention aids. It is probable that in this case the possibilities for retention by the bridging mechanism (7) overshadow the effects of steric stabilization at moderate dosages.

Paper mill effluent which contains starch is often difficult to clarify. The same protective colloid effect of the starch adsorbed on the suspended solids causes them to resist flocculation and sedimentation. In such cases neither alum

nor polymeric flocculants in economical dosages are effective (8). However, some success has been claimed with the use of bentonite clay with or without an anionic polymer (8).

Recent studies (9) have shown that loss of pigment retention due to the presence of starch in the wet end can be completely overcome by the use of a large overdose of cationic polymer retention aids. For most mills such dosages would probably not be economically feasible. An overall economic analysis, including the benefits of improved saveall and clarifier operation in addition to improved first pass retention, might show advantages in some cases.

An alternative solution to the problem was suggested by Wilhelm's studies (5). He showed that the dispersing ability of starch for TiO_2 was proportional to its molecular size. He varied this size by treating the starch for different periods of time with an enzyme, α-amylase. This enzyme attacks the starch molecule at random causing hydrolysis of the backbone and rapid reduction of the molecular weight. Thus, a size reduction indicated by a decrease in starch solution Brookfield viscosity from 440 to 20 cp increased the amount of starch required to cause a given level of turbidity in a standard white water after settling by a factor of fifteen (5). The particular advantage of using an enzyme, amylase, to attack the starch is its specificity for that material. Unlike the nonspecific attack of acids, for example, the enzyme has no effect on cellulose, hemicellulose, or the gums.

Since Wilhelm's work, two applications of this concept have appeared (10,11). In one case (10), broke surface-sized with enzyme-converted starch was the source of the starch. The stock was treated with enzyme in the hydrapulper where virgin fiber and broke were mixed. When this treatment was instituted

the primary clarifier effluent's average turbidity decreased as did the incidence of system upsets. Schwonke and Davis also inferred an increase in paper machine retention with the treatment since clarifier inlet turbidities and clarifier inlet solids decreased. When cationic starch was used as the surface size the point of enzyme treatment was changed to take advantage of this starch's greater substantivity to the pulp. Enzyme was added to the sewer sump where the machine discharges are collected prior to transfer to the primary clarifier. Improvements in clarifier efficiency were noted here also.

In the second study (11) samples of effluent from a book mill were screened to remove the long fiber and treated with enzyme and alum to improve flocculation. The amount of alum required to achieve a given suspended solids removal was considerably reduced. The effects of pH, time, and type of enzyme were also optimized for the particular system.

The emphasis in these studies (10,11) was directed toward the improvement in clarifier operation by reducing the dispersing character of starch. In the present work the major interest is in the effects of the enzyme treatment on paper machine and saveall operation and on sheet properties. This report discusses background laboratory work to establish operating conditions. An exploratory mill trial is then briefly described followed by the major topic, the full-scale mill trial. Finally, an economic analysis is presented and possible applications to other mills are discussed.

LABORATORY STUDIES

In order to maximize the probability of a successful mill trial, a mill was sought with the following characteristics:

a) The only starch in the paper was that added as a surface size at the size press. Thus, only the broke needed to be subjected to the enzyme treatment. Carry over of enzyme to the wet end would not be harmful to other components of the furnish.

b) A suitable place for the broke treatment was necessary. This required the capability of controlling the reaction time, the pH, and possibly the temperature.

c) The machine on which the trial was being made should be independent of the others in the mill. That is, savealls, white water systems, and hydrapulpers should not be shared. This would allow a clearer analysis of the results.

d) The mill should be relatively close to the Institute so that the costs and logistics in the transportation of manpower and samples would not be problematical.

e) Finally, and most importantly, the wholehearted support of the mill personnel in planning and cooperating in the mill trial was crucial to its success.

Fortunately, a nearby mill was located which met these criteria. Trials were planned, and samples of their broke were obtained for laboratory assessment of the feasibility of the enzyme treatment. The broke samples were also used to determine the optimum conditions for the enzyme catalysis of the starch degradation.

EFFECT OF CONSISTENCY

For assessing the degree of starch degradation occurring under particular experimental conditions, an indirect test was used. This was an end-use oriented test. Handsheets were prepared under standard conditions, and titanium dioxide retention in the sheet was used as a measure of the amount of protective colloid effect afforded by the starch.

A sample of the mill broke containing about 12% starch based on the o.d. pulp was treated with enzyme at particular conditions of time, temperature, pH, and consistency. After treatment the broke was mixed with an equal amount of a bleached kraft softwood pulp having a freeness of 445 mL CSF. Titanium dioxide (5% on o.d. pulp) and 2.2% alum were added. Two-gram handsheets (62 g/m^2) were formed at 0.3% consistency and a pH of 5.0 in a Rapid Kothen sheet mold. The sheets were ashed and the retention of the total ash (TiO_2 added plus broke ash) was calculated.

The α-amylase chosen for these studies was Rapidase 720 (G B Fermentation Industries Inc., Des Plaines, IL). This product is furnished as a dilute solution of the enzyme for easy use. It is sold primarily as a desizing agent to the textile industry. The results of this report show it also to be quite effective for the proposed use in broke treatment.

Wu (11) worked with effluent samples containing about 0.1% suspended solids and 5-10% starch based on these solids. He found enzyme treatment for 15-30 minutes was adequate to improve the ability of alum to flocculate these samples.

Since we planned to treat the broke in the hydrapulper at a much higher solids content, we were interested in the effect of consistency on the effectiveness of the treatment. Samples of the mill broke at either 0.5 or 5% consistency were treated with the enzyme for two hours at room temperature and a pH of 6.5. Four levels of enzyme concentration from 5 to 40% by weight of enzyme solution on weight of the starch were used at each consistency. The treated samples were mixed with the other components as described above, and the ash retention in handsheets was determined.

The average retention of ash with treatment at 5 and 0.5% consistency was 87 and 74%, respectively. No effect of enzyme dosage level was noted over the range covered. Since the samples during treatment were only stirred occasionally over the two-hour period, the difference between the two consistencies can be attributed to a diffusion effect. Evidently, the diffusion of starch to enzyme or vice versa is the rate-limiting step in the reaction. The higher consistency reduces the diffusion path length and results in more effective treatment. Further support for diffusion being the limiting factor will be adduced from the results of the effect of temperature discussed below. From the evidence of the experiment above, it appears that the starch degradation proceeds without problems at broke hydrapulper consistencies.

EFFECT OF ENZYME CONCENTRATION

Without knowing the enzyme activities of the previously published studies (10,11), it is not possible to predict the dosages required in the present work. Accordingly a wide range of enzyme concentrations were tested for their effectiveness. Based on the amount of starch in the broke, weight percents of enzyme solution from 1 to 33% were mixed with the broke for one hour at pH 6.5 and room

temperature. As before, the treated broke was then mixed with the other components, handsheets were formed, and ash retention was determined. The results are shown as percent retention against enzyme dosage in Fig. 1. At 8% and higher dosages a plateau in retention of about 77% is reached. This is a striking increase over the value of 28% with no enzyme treatment. Even small dosages of 1-2% enzyme on starch provide considerable improvement in retention.

EFFECT OF pH

The effect of pH on the enzyme degradation of starch was examined for two reasons. First, it was necessary to know the optimum pH so that the enzyme dosage could be minimized. Second, experiments at lower pH provided information about the rates of retention to be expected when the pH of the treated broke was decreased as it was mixed with the virgin pulp slurry in the main pulper.

Enzyme treatment of the mill broke was carried out at various pH's between 5 and 8. For this study a constant enzyme dosage of 2% based on the starch was used. The mixing time was one hour at room temperature. After treatment the broke was mixed with the other components as discussed above, formed into handsheets, and analyzed for retention of ash. The results are shown in Fig. 2 as percent retention plotted against pH. The optimum pH is in the range 7.5-7.7. In this range the retention is 75% which can be compared with a value of 77% at pH 6.5 using dosages of 8% or higher (Fig. 1). Because a dosage of 2% at pH 7.5 gives good retention at a relatively modest cost, these conditions were chosen to be used during the second mill trial.

The rate of enzyme reaction decreases markedly at lower values of pH. Indeed, at pH 5 the same retention (28%) was obtained as in the case with no

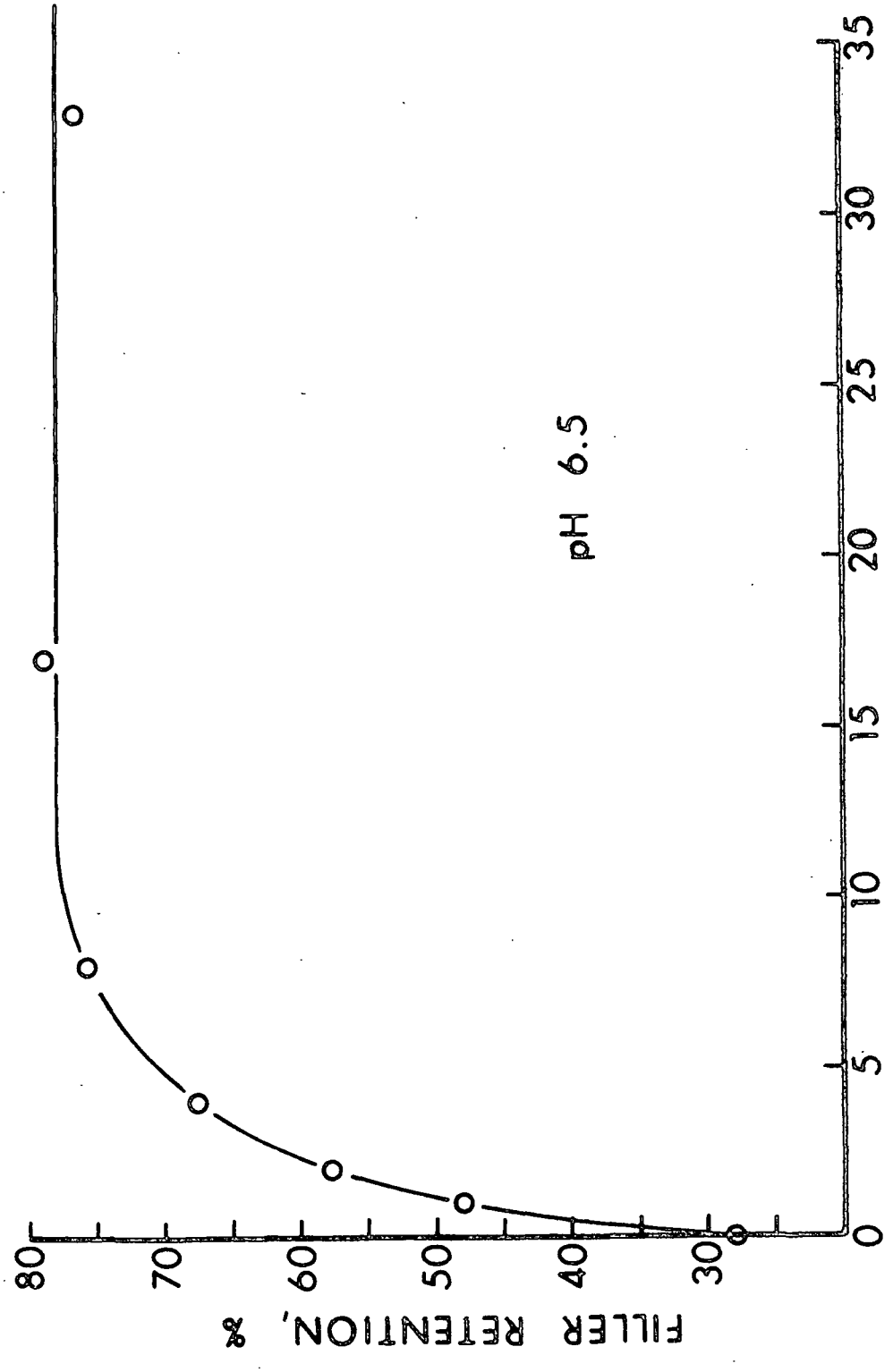

Figure 1. Effectiveness of Enzyme as a Function of its Concentration

enzyme treatment (Fig. 1). This suggests that little further reaction will take place once alum has been added to the stock.

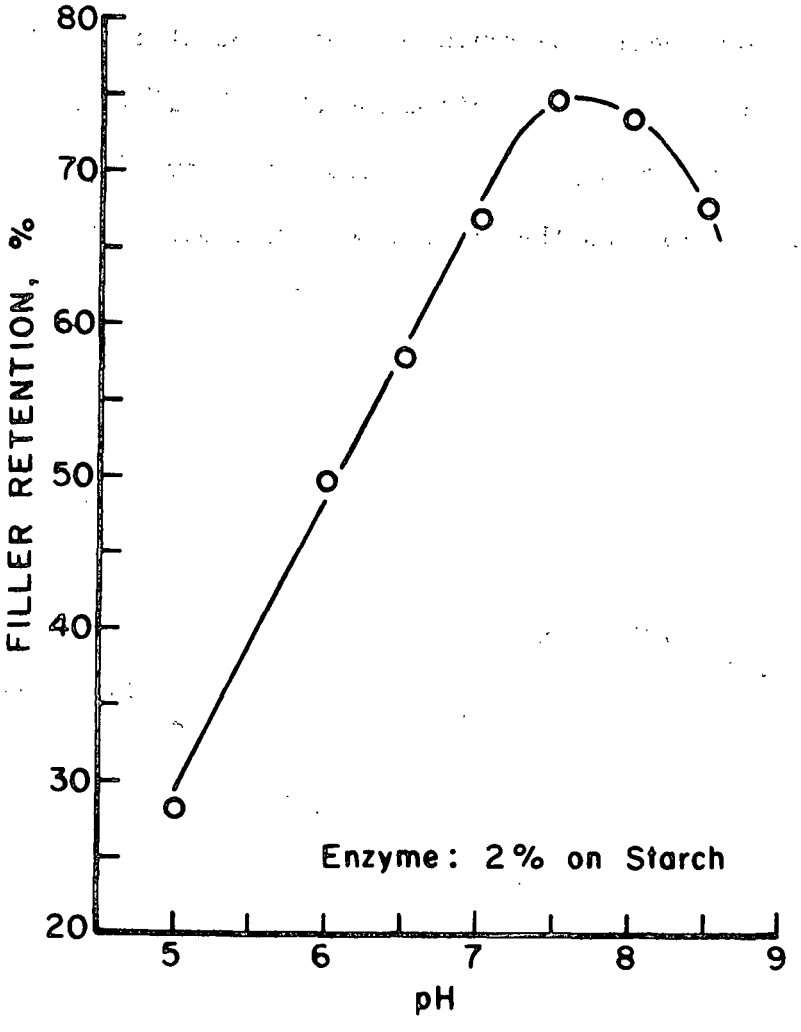

Figure 2. Effectiveness of Enzyme as a Function of pH

EFFECT OF TEMPERATURE

It was expected that some advantage in reaction rates might be obtained by operating at higher temperatures. Experiments were carried out over a range of temperatures from 23 to 85°C (73 to 185°F). The broke was agitated continuously for one hour at the given temperature. An enzyme dosage of 2% based on

the starch and a pH of 6.5 were employed. After treatment, the broke temperature was lowered to that of the room, and handsheets were made and analyzed as before. The results are shown in Fig. 3. Apparently, temperature has little or no effect on the rate of the reaction in the range covered. (Still higher temperatures are known to denature the enzyme.) This means that the addition of steam to the hydrapulper to facilitate repulping will probably not have an adverse effect on the enzyme treatment so long as the broke temperature does not exceed 85°C.

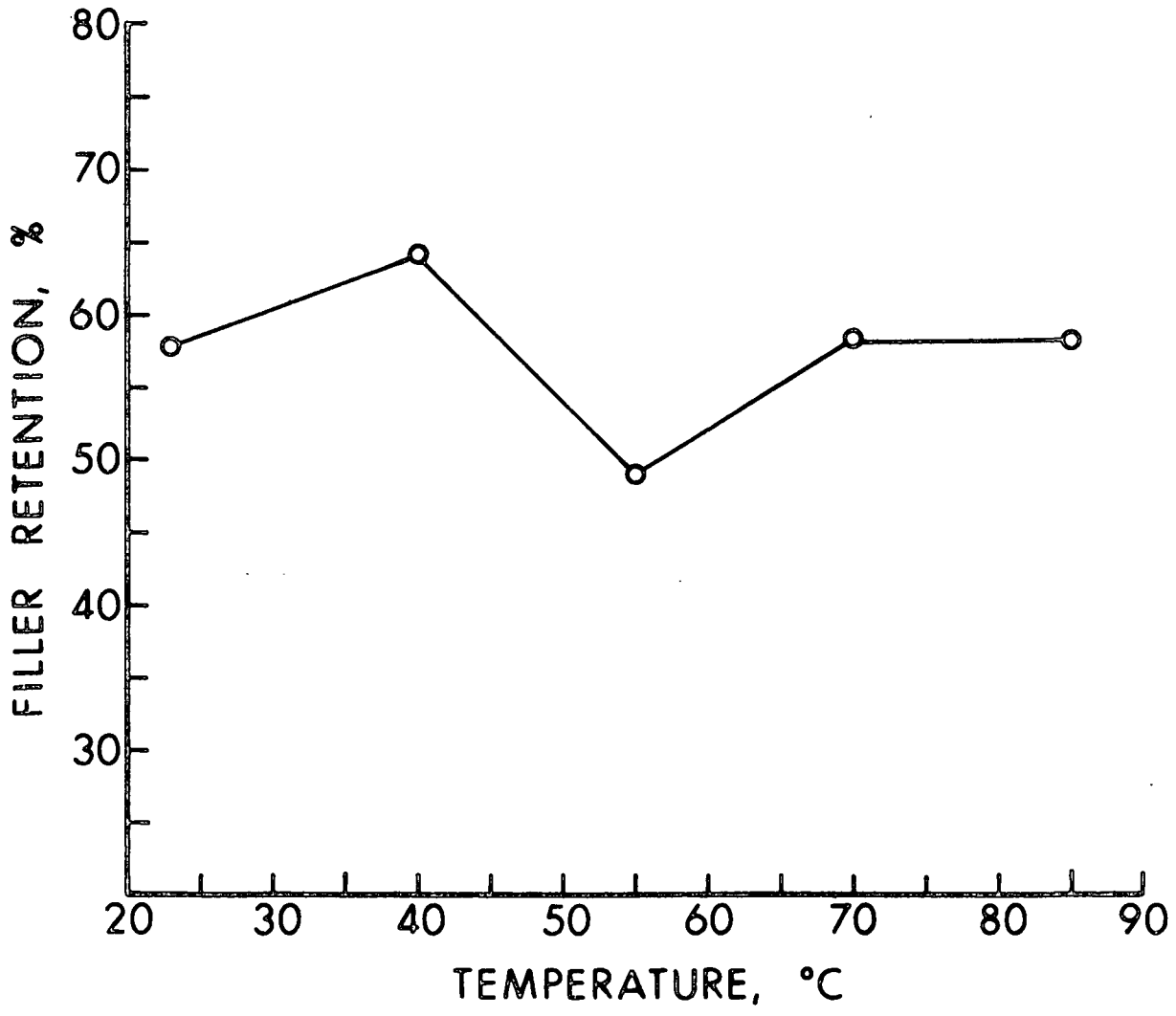

Figure 3. Effectiveness of Enzyme as a Function of Temperature

The lack of a consistent increase in reaction rate with increasing temperature suggests that diffusion of the reactants rather than an activation energy is the rate-limiting step. Diffusion is directly proportional to the absolute temperature which only increases 20% from 23 to 85°C. This observation concurs with the effect of consistency noted earlier.

The effect of temperature on the enzyme has one further ramification. This concerns the eventual fate of the enzyme. It is important that the enzyme be denatured by the time it reaches the size press. Otherwise, active enzyme might be leached from the sheet into the starch size slurry and bring about hydrolysis of this material. The result would be a loss in sizing. The simplest method of enzyme denaturation is to raise the temperature to or near to the boiling point for a brief period of time. The specific time and temperature requirements are crucial to the question of whether the enzyme will be irreversibly inactivated during passage through the driers prior to the size press.

Two experiments were conducted in the laboratory to simulate the drying conditions on a machine. Handsheets from stock containing starch and enzyme were made on a Rapid Kothen sheet mold and were pressed as usual. They were dried either on a drum drier at 105°C for 1, 2, 4, or 7 minutes or between 60-mesh stainless steel wires on a hotplate at 375°C for 15, 25, 45, or 90 seconds. Sheets dried for 1 and 2 minutes and for 15 and 25 seconds by the respective methods were not completely dry. For these, drying was completed by air-drying on TAPPI drying rings. Portions of the dried sheets were soaked in buffer solution. Samples of the latter were then tested for active α-amylase using the Radial Diffusion Assay method (Worthington Biochemical Corporation, Freehold, NJ). Only the sample dried for 15 seconds on the hotplate showed any activity. It was concluded that passage through the driers before the

size press should be sufficient to denature the enzyme. Experience during the mill trials bore out this finding. No problems were encountered due to active enzyme.

With the background information from the laboratory in hand, we were ready to try the treatment in the mill.

FIRST MILL TRIAL

The first mill trial was conceived to be exploratory in nature. Therefore, rather unrealistic enzyme dosages of about 20 and 100% based on the estimated amount of starch in the broke were used at a pH of 6.5. These values are well out into the plateau region (see Fig. 1) and should produce a marked effect on the protective colloid function of the starch. We purposefully used a large overdose of enzyme for the initial trial because we were uncertain how the treatment would work under mill conditions.

A fuller description of the system will be presented in the next section. As expected the effect of starch in the wet end during the enzyme treatment disappeared. First pass retention of TiO_2 and of total ash increased substantially along with a slight increase in opacity. The most dramatic change was in the efficiency of operation of the saveall. Before the enzyme treatment was begun, the clear leg of the saveall was quite turbid. During the course of several hours of treatment this stream gradually cleared until it reached the appearance of fresh water. This was a striking illustration of the effect starch has on saveall operation.

Previous workers (10,11) have shown that treatment with enzyme increases the BOD load in the effluent. This is because some of the starch that is substantive to the fiber will remain with the sheet in the untreated case. Reaction with the enzyme converts this starch (along with that suspended in the white water) to small fragments which end up in the effluent (10). In a like manner some of the starch entering a primary clarifier will be adsorbed on settleable particles. Upon treatment with enzyme, this starch is degraded to fragments which stay in solution and increase the BOD of the effluent from the primary clarifier (11).

For the present study we were concerned about the magnitude of the increases in BOD as they would affect the economics and environmental impact of the treatment. A suitable stream in the mill for BOD analysis was the rejects from the tertiary cleaners. The rejects are sewered along with the overflow from the clear leg of the saveall. The results of the BOD analysis are shown in Fig. 4 for the duration of the trial. Before treatment the average is about 700 mg/liter; enzyme treatment causes an increase to about 1000 mg/liter. Such a sizeable increase must be accounted for in the overall economic analysis of the system.

With a successful, albeit uneconomical, mill trial completed, another trial to establish the economic feasibility of the enzyme treatment was planned.

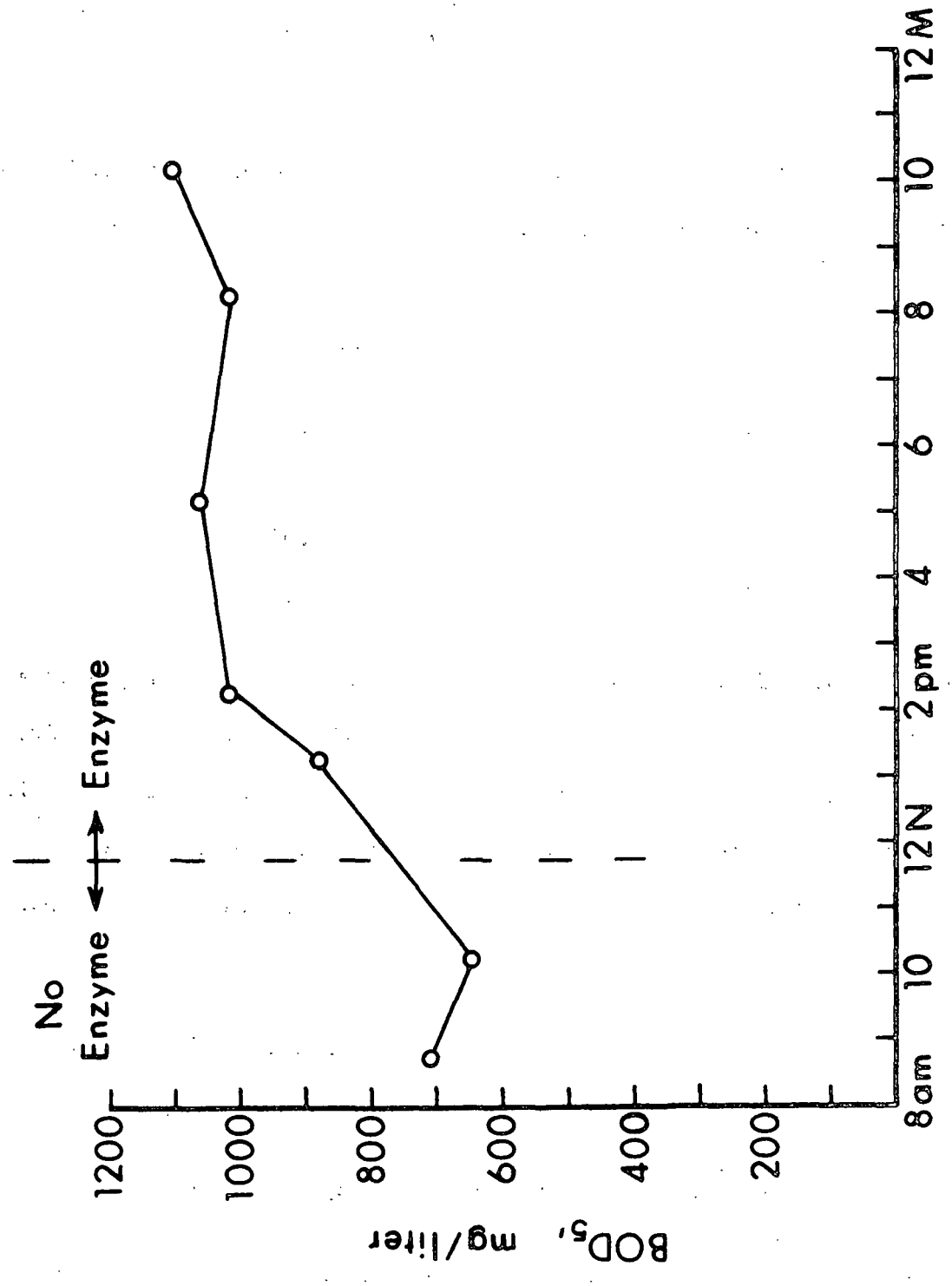

Figure 4. BOD_5 of Rejects from Tertiary Cleaners (First Mill Trial)

SECOND MILL TRIAL

DESIGN

The trial was carried out over a period of 24 hours. It can be broken into four segments of approximately six hours each as follows.

Time, hr	Enzyme Treatment	Retention Aid Dosage, lb/ton
6	No	0.33
6	Yes	0.33
6	Yes	0.07
6	No	0.07

This schedule provided first a base line, then a period for the enzyme treatment to take effect. Midway through the trial, the retention aid dosage was drastically reduced to determine whether savings could be achieved here. Finally, a period to provide base-line data for the reduced retention aid dosage was included. This segment also gave information on how fast the system responded to the removal of the enzyme treatment.

The approximate clock times for the demarcation of the four segments can be identified as follows:

a) The trial began at 10:00 p.m. following a grade change.

b) The first pulper load containing some enzyme treated broke was dropped to the cycle chest about 1:30 a.m. Based on the system flows, this pulp should have reached the slice about 2:00 a.m.

c) The retention aid dosage was cut just before 9:30 a.m. Samples collected at 9:30 a.m. and later were under the influence of the lower dosage.

d) The last charge of treated broke was dropped from the hydrapulper to the broke chest at 1:55 p.m. The last furnish containing this broke reached the machine about 4-6 p.m.

The results of the various analyses reported below help to fix these demarcation times more clearly.

EXPERIMENTAL

The Papermaking System

The grade of paper chosen for the trial was a moderately filled sheet containing about 8-9% ash. About one-third the ash was TiO_2, the remainder being a hydrated amorphous silica extender. The basis weight was 20 lb/ream (17 inches x 22 inches-500) or 75 g/m^2. The machine was run at 500 ft/min with foils as drainage elements. Starch surface sizing was applied at a size press. The pickup of the enzyme converted starch was about 3%.

White water not used for dilution of the thick stock at the fan pump was sent to the couch pit. Here it was mixed with sweetener stock from the machine chest before being sent to a disc saveall. The clear leg of the latter was used in stock preparation and as shower water.

The stock was a mixture of hardwood and softwood bleached kraft pulps, cotton linters, and repulped broke. The last-named comprised about 30% of the pulp. Internal size, optical brightener, and alum were also added to the main pulper. A dilute solution of an anionic polymer retention aid (at a dosage

rate of 0.33 or 0.07 lb/ton) was added after the pressure screens (just before the headbox).

White broke averaging about 6% starch was repulped in a hydrapulper in batches of about 2400 pounds. The starch was a mixture of hydroxyethylated and enzyme-converted products. Before addition of enzyme, the pH in the hydrapulper was adjusted to 7.5 with sodium aluminate. A total of seven batches of the broke were each treated with 1.36 liters of neat Rapidase 720. Assuming an average of 6% starch this amount was equivalent to a 2% by weight dosage of enzyme on the starch. The residence time in the hydrapulper after enzyme addition was one-half to one hour. The batch was then dropped to the broke chest where it was diluted to about 3-1/2% consistency. At this time the pH was decreased away from the optimum but some further reaction of enzyme and starch probably occurred before the broke was used for stock makeup.

Sampling: Locations and Times

To monitor the effect of the enzyme treatment, samples were periodically collected from a number of locations during the trial.

- Stuffbox
- Headbox
- Tray water (composite white water from all foils)
- Saveall clear leg
- Rejects from tertiary cleaners
- Paper

Headbox, white water, and paper samples were used in the calculation of first pass retention. Saveall clear leg samples gave an indication of its operating efficiency. As mentioned previously, the overflow from the saveall clear leg

and the rejects from the tertiary cleaners are the major streams being sewered by this mill. These two samples, then, gave a measure of the amounts and kinds of materials being lost in the operation. The stuffbox sample was analyzed for starch to ascertain when enzyme treated broke reached the paper machine wet end. To minimize further enzyme reaction in these stuffbox samples after collection, the pH was immediately adjusted to 3.0 with hydrochloric acid.

Sampling times were chosen to coincide with the turnup of a reel of paper so that paper and wet end samples could be correlated.

In addition samples of each batch of broke in the hydrapulper during the trial were taken. For those batches to which enzyme was added, the samples were collected before pH adjustment and enzyme addition.

Analyses

Approximately one liter of each of the wet end samples was collected. A known volume (or weight for the high consistency samples) of each sample was filtered through a tared No. 42 Whatman ashless filter paper under vacuum. The filter papers were oven-dried, weighed, ashed at 840°C for two hours and reweighed. The amount of solids and of ash were calculated as grams/100 mL (or g/100 g). The ashed sample was analyzed for TiO_2 according to the volumetric procedure in TAPPI Method T 439 m-60. Results are reported as grams TiO_2/100 mL (or per 100 g). Selected samples of the saveall clear leg were similarly treated using, however, 0.1 μm Millipore membranes instead of the filter paper.

Because the amount of solids in the saveall clear leg was very low, the above procedure for solids and ash was not used for most of the samples. Instead the intensity I of a white light beam passing through a cell containing the sample

was measured immediately after sample collection and compared with the intensity I_o of the beam passing through distilled water. The apparatus, which uses a silicon solar cell as the detector and a microammeter as the readout device, has been previously described (12). The turbidity τ was calculated from

$$I = I_o e^{-\tau x}$$

where x is the path length through the cell (1.6 cm). Results (12) for suspensions of TiO_2 show that the turbidity is directly proportional to the concentration of TiO_2 for values of the latter of 50 ppm or less (or, equivalently, for values of τ less than 0.6). At higher concentrations direct proportionality no longer holds due to secondary scattering, but measurements can be made up to 1000 ppm TiO_2 (or $\tau = 3$).

The conductivity and electrophoretic mobility of the supernatant from portions of selected headbox samples which had been allowed to settle under gravity were measured with a Zeta-Meter (Zeta-Meter Inc., New York, NY). The electrophoretic mobility of the particles (pigment and pulp fines) was converted to zeta potential using the Smoluchowski equation (13).

The pH of each wet end sample was measured with a Beckman pH Meter, Model N, which had been standardized with pH 4 buffer.

The biological oxygen demand (BOD_5) of the samples of rejects from the tertiary cleaners was measured according to the standard method (14).

Starch in the broke and stuffbox samples was determined according to the standard method for paper samples (15). Because the samples contain a mixture of starch and its hydroxyethylated derivative, absolute concentrations cannot be calculated. Instead, only the optical absorbance at 580 nm of the starch-iodine

complex is reported. Since the ratio of the two starches may vary from sample to sample, and since the absorptivities of the two starches are different, it is likely that only large changes in the reported values have significance.

Paper properties were measured by the cooperating mill as part of their quality control program. These included basis weight, caliper, burst (Mullen), tear, fold, brightness, and opacity. Only opacity will be reported here since the other properties were invariant with the enzyme treatment.

Additional optical properties and composition were measured at the Institute. Specific scattering and absorption coefficients were calculated using the Kubelka-Munk theory from transmission and reflectance measurements taken on a General Electric Recording Spectrophotometer at a wavelength of 650 nm. The amount of ash and of TiO_2 in the paper samples was determined as described above for the wet end samples. The results are reported as the percent of the oven-dried weight.

RESULTS

The data for the pH, starch test absorbance (where applicable), and amounts of solids, ash, TiO_2, and fiber in the wet end samples are listed in Tables I-V. The value for "fiber" is given by the difference between those for "solids" and "total ash." The percent ash is the ratio of "total ash" to "solids" converted to a percentage. The results for the pH and turbidity of the saveall clear leg are given in Table VI. Values for solids, ash, TiO_2, and fiber for selected samples of this stream are presented in Table VII.

TABLE I

BROKE HYDRAPULPER

Time Variation of Composition

Sampling Time	Solids, g/100 g	Total Ash, g/100 g	TiO_2, g/100 g	Fiber, g/100 g	Ash, %	pH	Starch, absorbance
9:50 p.m.	6.68	0.345	0.010	6.34	5.2	4.8	0.094
12:15 a.m.[a]	7.37	0.301	0.014	7.07	4.1	3.9	--
2:00[a]	8.72	0.595	0.058	8.12	6.8	4.9	0.073
4:30[a]	7.51	0.438	0.096	7.07	5.8	3.8	0.076
5:45[a]	8.53	0.701	0.088	7.83	8.2	4.9	0.073
8:10[a]	8.45	0.668	0.086	7.78	7.9	5.6	0.056
9:50[a]	5.86	0.417	0.035	5.44	7.1	5.4	0.065
1:15 p.m.[a]	6.92	0.169	0.009	6.75	2.4	4.8	0.044
4:15	6.23	0.417	0.080	5.82	6.7	5.1	0.072
5:55	6.66	0.796	0.057	5.87	12.0	5.3	0.089
7:40	7.14	0.407	0.026	6.74	5.7	5.3	0.089

[a]Enzyme was added to these batches after collection of the sample.

Results for the conductivity of selected headbox samples taken throughout the trial ranged from 790 to 830 micromhos/cm. There was no systematic trend with respect to time of sampling.

The zeta potentials for these same headbox samples was smaller in magnitude than 3 mv. For most of the samples no movement (zero zeta potential) was observed, while for some a slight indication of a negative zeta potential (unmeasurable) was visible.

TABLE II

STUFFBOX

Time Variation of Composition

Sampling Time	Solids, g/100 g	Total Ash, g/100 g	TiO_2, g/100 g	Fiber, g/100 g	Ash, %	Starch, absorbance
10:35 p.m.	3.32	0.371	0.092	2.95	11.2	0.031
11:15	3.47	0.419	0.118	3.06	12.1	0.044
12:15 a.m.	3.70	0.395	0.121	3.30	10.7	0.034
12:45	3.46	0.411	0.124	3.05	11.9	0.039
1:40	3.38	0.414	0.129	2.97	12.3	0.036
2:30	3.44	0.408	0.103	3.04	11.8	0.028
3:20	3.11	0.352	0.120	2.76	11.3	0.014
4:05	2.99	0.351	0.135	2.64	11.7	0.049
4:50	3.32	0.387	0.123	2.93	11.7	0.025
5:35	3.35	0.392	0.123	2.96	11.7	0.021
6:40	3.47	0.407	0.132	3.07	11.7	0.020
7:30	3.33	0.383	0.127	2.94	11.5	0.021
8:20	3.33	0.380	0.130	2.95	11.4	0.000
9:30	3.36	0.384	0.117	2.98	11.4	0.007
10:25	3.62	0.424	0.130	3.20	11.7	0.018
11:25	3.44	0.406	0.125	3.03	11.8	0.004
12:15 p.m.	3.45	0.412	0.127	3.03	12.0	0.010
1:00	3.46	0.412	0.125	3.05	11.9	0.011
1:50	3.42	0.428	0.105	2.99	12.5	0.009
2:45	3.46	0.415	0.118	3.05	12.0	0.009
3:25	3.56	0.406	0.123	3.15	11.4	0.013
4:10	3.42	0.377	0.121	3.04	11.0	0.015
5:00	3.35	0.366	0.120	2.99	10.9	0.008
6:00	3.33	0.359	0.118	2.97	10.8	0.024
7:00	3.39	0.368	0.116	3.02	10.9	0.019
7:55	3.29	0.390	0.098	2.90	11.9	0.047
9:00	3.43	0.419	0.107	3.01	12.2	0.065

TABLE III

TERTIARY CLEANER REJECTS

Time Variation of Composition

Sampling Time	Solids, g/100 mL	Total Ash, g/100 mL	TiO_2, g/100 mL	Fiber, g/100 mL	Ash, %	pH
10:35 p.m.	0.478	0.160	0.079	0.318	33.5	5.4
11:15	0 446	0.156	0.076	0.290	35.0	5.3
12:15 a.m.	0.365	0.129	0.064	0.236	35.3	5.2
12:45	0.363	0.130	0.064	0.233	35.8	5.6
1:40	0.363	0.127	0.059	0.236	35.0	5.8
2:30	0.378	0.123	0.070	0.256	32.4	5.6
3:20	0.371	0.106	0.058	0.266	28.5	5.8
4:05	0.381	0.108	0.063	0.273	28.4	5.7
4:50	0.362	0.102	0.059	0.260	28.2	5.7
5:35	0.350	0.096	0.053	0.255	27.3	5.6
6:40	0.340	0.089	0.055	0.252	26.1	5.7
7:30	0.326	0.088	0.056	0.238	26.9	5.7
8:20	0.314	0.083	0.055	0.231	26.4	5.6
9:30	0.298	0.088	0.052	0.209	29.7	5.4
10:25	0.327	0.106	0.063	0.221	32.5	5.4
11:25	0.345	0.108	0.066	0.238	31.2	5.2
12:15 p.m.	0.293	0.094	0.059	0.199	32.2	5.4
1:00	0.354	0.116	0.069	0.238	32.9	5.6
1:50	0.326	0.098	0.055	0.228	30.1	5.7
2:45	0.345	0.124	0.067	0.221	35.9	5.7
3:25	0.345	0.104	0.066	0.241	30.2	5.7
4:10	0.357	0.105	0.070	0.252	29.3	5.5
5:00	0.334	0.087	0.058	0.248	25.9	5.5
6:00	0.304	0.092	0.054	0.212	30.3	5.5
7:00	0.340	0.120	0.057	0.221	35.2	4.7
7:55	0.359	0.136	0.048	0.223	38.0	5.4
9:00	0.357	0.143	0.053	0.213	40.2	5.0

TABLE IV

HEADBOX

Time Variation of Composition

Sampling Time	Solids, g/100 mL	Total Ash, g/100 mL	TiO_2, g/100 mL	Fiber, g/100 mL	Ash, %	pH
10:35 p.m.	0.844	0.131	0.036	0.712	15.6	5.2
11:15	0.910	0.154	0.050	0.756	16.9	5.1
12:15 a.m.	0.869	0.146	0.052	0.723	16.7	5.1
12:45	0.858	0.143	0.050	0.715	16.6	5.0
1:40	0.826	0.135	0.048	0.692	16.3	5.0
2:30	0.810	0.127	0.046	0.683	15.6	5.2
3:20	0.803	0.115	0.041	0.689	14.3	5.2
4:05	0.785	0.112	0.041	0.673	14.3	5.1
4:50	0.843	0.113	0.041	0.731	13.3	5.0
5:35	0.796	0.114	0.039	0.683	14.3	4.9
6:40	0.769	0.105	0.037	0.664	13.7	5.0
7:30	0.768	0.103	0.037	0.665	13.4	5.1
8:20	0.771	0.100	0.036	0.671	13.0	5.0
9:30	0.726	0.105	0.038	0.621	14.6	5.0
10:25	0.825	0.119	0.041	0.706	14.4	5.2
11:25	0.802	0.114	0.037	0.689	14.2	4.9
12:15 p.m.	0.835	0.119	0.041	0.716	14.2	4.8
1:00	0.868	0.126	0.047	0.742	14.5	5.0
1:50	0.853	0.124	0.041	0.729	14.5	4.9
2:45	0.839	0.122	0.042	0.717	14.6	4.9
3:25	0.831	0.113	0.037	0.718	13.6	5.1
4:10	0.854	0.112	0.039	0.742	13.1	4.9
5:00	0.770	0.099	0.037	0.671	12.9	4.9
6:00	0.777	0.096	0.036	0.681	12.4	4.7
7:00	0.844	0.101	0.039	0.744	11.9	4.6
7:55	0.859	0.114	0.034	0.745	13.3	4.3
9:00	0.882	0.132	0.041	0.750	15.0	4.1

TABLE V

TRAY WATER

Time Variation of Composition

Sampling Time	Solids, g/100 mL	Total Ash, g/100 mL	TiO_2, g/100 mL	Fiber, g/100 mL	Ash, %	pH
10:35 p.m.	0.178	0.078	0.024	0.100	43.9	4.8
11:15	0.191	0.090	0.032	0.102	47.0	4.8
12:15 a.m.	0.205	0.089	0.034	0.116	43.6	4.9
12:45	0.191	0.081	0.031	0.110	42.5	4.8
1:40	0.181	0.075	0.028	0.105	41.7	4.7
2:30	0.170	0.066	0.026	0.104	39.0	4.8
3:20	0.153	0.055	0.021	0.098	35.9	5.0
4:05	0.145	0.053	0.019	0.093	36.3	4.8
4:50	0.156	0.055	0.019	0.101	35.1	4.9
5:35	0.152	0.053	0.018	0.099	34.9	4.9
6:40	0.103	0.041	0.014	0.062	39.6	4.6
7:30	0.098	0.038	0.014	0.059	39.2	4.6
8:20	0.100	0.038	0.014	0.062	38.1	4.9
9:30	0.136	0.046	0.016	0.089	34.2	4.9
10:25	0.142	0.056	0.018	0.086	39.6	4.9
11:25	0.144	0.055	0.017	0.089	38.5	4.9
12:15 p.m.	0.142	0.056	0.018	0.086	39.5	4.8
1:00	0.141	0.058	0.018	0.083	41.0	4.9
1:50	0.138	0.057	0.015	0.081	41.5	4.9
2:45	0.144	0.058	0.017	0.086	40.2	4.9
3:25	0.142	0.055	0.017	0.087	38.5	4.9
4:10	0.134	0.048	0.016	0.086	35.7	4.9
5:00	0.126	0.042	0.015	0.084	33.6	4.8
6:00	0.132	0.042	0.016	0.090	31.8	4.4
7:00	0.152	0.051	0.019	0.100	33.9	4.2
7:55	0.159	0.060	0.019	0.099	37.8	3.8
9:00	0.179	0.076	0.023	0.103	42.7	3.7

TABLE VI

SAVEALL CLEAR LEG TURBIDITY

Sampling Time	Turbidity	pH
10:35 p.m.	1.064	4.5
11:15	1.535	--
12:15 a.m.	1.872	--
12:45	1.829	5.3
1:40	1.789	5.4
2:30	1.248	--
3:20	0.844	--
4:05	0.835	5.2
4:50	0.606	--
5:35	0.468	--
6:40	0.366	--
7:30	0.333	--
8:20	0.305	5.2
9:30	0.357	--
10:25	0.294	--
11:25	0.229	--
12:15 p.m.	0.212	--
1:00	0.224	--
1:50	0.185	--
2:45	0.175	5.1
3:25	0.168	--
4:10	0.190	--
5:00	0.212	--
6:00	0.295	--
7:00	0.383	--
7:55	0.549	--
9:00	0.839	--
10:00	1.439	--

TABLE VII

SAVEALL CLEAR LEG

Time Variation of Composition

Sampling Time	Solids, g/100 mL	Ash, g/100 mL	TiO_2, g/100 mL	Fiber, g/100 mL
12:45 a.m.	0.0293	0.0235	0.0136	0.0058
8:20 a.m.	0.0040	0.0022	0.0018	0.0018

The BOD values on the samples from the rejects of the tertiary cleaners were meaningless. Measurements on the same sample at different levels of dilution produced widely scattered results without the usual expected trend. Unlike the data presented in Fig. 4 for the first trial, no clear trends could be discerned because of the scatter. Apparently, some factor was present which interfered with the test throughout the duration of the second trial.

Values for the percent ash, percent TiO_2, opacity, and specific scattering coefficient for the paper samples are listed in Table VIII. The magnitude for the specific adsorption coefficient for these samples was low (0.65-0.99) as would be expected with a well-bleached pulp.

First pass retention of ash and of TiO_2 was obtained by comparison of the ash (TiO_2) in the sheet to the ash (TiO_2) in the headbox with both normalized to unit weight of fiber.

$$\% \text{ R (ash)} = (100)\left(\frac{\% \text{ Sheet Ash}}{100-\% \text{ Sheet Ash}}\right)\Big/\left(\frac{\text{Headbox Ash}}{\text{Headbox Fiber}}\right)$$

$$\% \text{ R } (TiO_2) = (100)\left(\frac{\% \text{ Sheet } TiO_2}{100-\% \text{ Sheet Ash}}\right)\Big/\left(\frac{\text{Headbox } TiO_2}{\text{Headbox Fiber}}\right)$$

The results of these calculations are listed in Table IX.

TABLE VIII

PAPER

Time Variation of Composition and Optical Properties

Sampling Time	Total Ash, %	TiO_2, %	Opacity	Specific Scattering Coefficient, cm^2/g
10:30 p.m.	7.88	1.69	91.2	557
11:40	7.46	2.28	91.2	628
12:30 a.m.	7.53	2.31	91.4	605
1:30	8.64	2.86	91.4	663
2:25	8.78	3.03	92.2	691
3:15	8.73	3.03	91.9	670
4:05	8.82	3.16	90.9	695
4:55	9.09	3.21	92.1	692
5:45	9.14	3.19	91.9	674
6:45	9.54	3.36	92.6	677
7:35	9.26	3.35	93.0	669
8:25	9.14	3.32	92.4	688
9:35	8.48	2.82	91.6	665
10:30	9.22	3.05	91.0	671
11:25	9.34	3.09	92.0	691
12:15 p.m.	9.17	3.05	91.9	683
1:00	9.24	3.08	92.0	641
1:45	9.20	3.06	92.5	645
2:45	9.30	2.88	91.7	692
3:25	8.74	2.95	92.0	678
4:05	8.75	2.86	92.0	668
4:50	8.34	2.91	92.0	663
5:55	8.31	3.09	92.5	689
6:55	8.21	2.98	92.0	657
7:50	7.58	2.72	90.6	639
8:25	8.14	2.38	90.6	633
9:00	8.08	2.28	91.7	616
9:35	8.09	2.40	91.7	637

TABLE IX

FIRST PASS RETENTION

Sampling Time	Ash, %	TiO_2, %	Solids, %	Fiber, %
10:35 p.m.	46.5	36.3	78.9	86.0
11:15	39.6	37.3	79.0	86.5
12:15 a.m.	40.3	34.7	76.4	84.0
12:45	40.7	35.7	77.7	84.6
1:40	48.5	45.1	78.1	84.8
2:30	51.8	49.3	79.0	84.8
3:20	57.3	55.8	81.0	85.8
4:05	58.1	56.9	81.5	86.2
4:50	64.6	63.0	81.5	86.2
5:35	60.3	61.5	80.9	85.5
6:40	66.7	66.7	86.6	90.7
7:30	65.9	66.4	87.2	91.1
8:20	67.5	68.1	87.0	90.8
9:30	54.8	50.4	81.3	85.7
10:25	60.2	57.9	82.8	87.8
11:25	62.2	63.5	82.0	87.1
12:15 p.m.	60.8	58.6	83.0	88.0
1:00	60.0	53.6	83.8	88.8
1:50	59.6	59.9	83.8	88.9
2:45	60.3	54.2	82.8	88.0
3:25	60.8	62.7	82.9	87.9
4:10	63.5	59.6	84.3	88.4
5:00	61.6	57.6	83.6	87.5
6:00	64.3	63.8	83.0	86.8
7:00	65.8	61.9	82.0	86.6
7:55	53.6	64.5	81.5	86.7
9:00	49.9	45.4	79.7	86.3

First pass retention of total solids and of fiber were calculated by comparing the amounts of these in the headbox and in the tray water.

$$\% R \text{ (solids)} = (\text{Headbox Solids} - \text{Tray Solids})(100)/(\text{Headbox Solids})$$

$$\% R \text{ (fiber)} = (\text{Headbox Fiber} - \text{Tray Fiber})(100)/(\text{Headbox Fiber})$$

The results are listed in Table IX.

DISCUSSION

In order to assess the effect of the enzyme, it was important to have an independent measure of when the treated broke was on the wire. This was done by determining the amount of starch in the stock at the stuffbox. The results are plotted in Fig. 5. During the base-line portion of the trial the optical absorbance was about 0.03-0.04. Upon treatment of the broke, the absorbance decreased to a value of about 0.01. Upon discontinuation of the treatment the absorbance rose again. As mentioned previously, the test is only a relative measure of the amount of starch because probably both the quantity and type of starch varied with time. The values for the absorbance of the starch in the hydrapulper (Table I) exhibited considerable batch-to-batch variation, again due to different amounts and types of starch in the broke. Thus, the point-to-point variation in Fig. 5 is also a reflection of the nonuniformity of the composition of the broke. Considering the overall trends in Fig. 5, one can conclude that enzyme-treated broke was in the stock at the headbox between about 2 a.m. and 6 p.m. It should be noted that, even during the treatment, there was still starch in the wet end. However, either the amount or the molecular size of the starch molecules was insufficient during treatment to cause serious problems with retention or saveall operation as reported below.

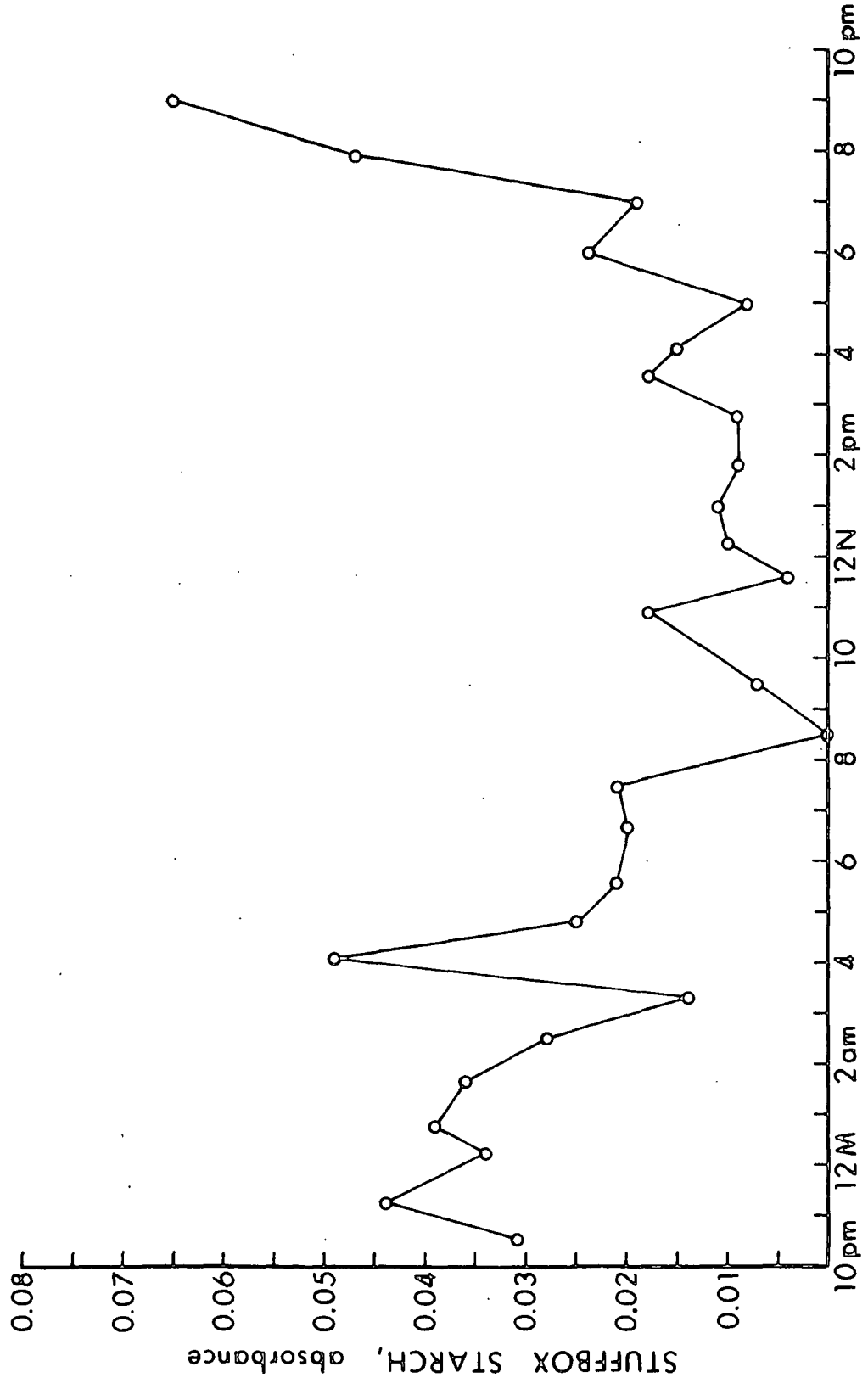

Figure 5. Variation in Amount of Starch in the Stuffbox Stock During Trial

Observation of the tray water can provide a good relative indication of the quality of retention. The concentrations of ash and fiber in the tray are individually plotted in Fig. 6. Both fiber and ash were reduced by the enzyme treatment — by about 20% and 35%, respectively. The low values (particularly for the fiber) at 6:40, 7:30, and 8:20 a.m. appear out of line with the rest of the data. Reruns of the analyses of these samples, however, confirmed the amounts shown. The effect of introduction of starch-containing broke into the wet end again is apparent after 6 p.m. in the values for the ash and to a lesser extent for the fiber.

Because the tray water was recycled, the changes shown in Fig. 6 are also mirrored in the amount of ash in the headbox stock displayed in Fig. 7. (The variations in headbox fiber — see Table IV — appeared to be independent of the enzyme treatment sequence.) There was a 30% decrease in headbox ash due to the treatment. After 6 p.m. a rise toward pretreatment levels is seen. A temporary reversal of the trend occurred at 9:30 a.m. corresponding to the reduction in retention aid dosage. This reduction would likely lead to lower first pass retention resulting in higher tray water concentrations followed by higher headbox ash. The effect of cutting the retention aid dosage is also apparent in Fig. 6. For both headbox and tray water the reversal in trend was only temporary. With continued enzyme treatment the system was able to adjust to the lower dosage of retention aid. It is likely that, had the higher level of retention aid been maintained throughout the trial, even lower concentrations of fines in the wet end would have been observed.

The rejects from the tertiary cleaners are composed of both fresh and recycled stock. Thus, changes in the ash content of the rejects might be expected to parallel those in the headbox. Such is the case as is shown in

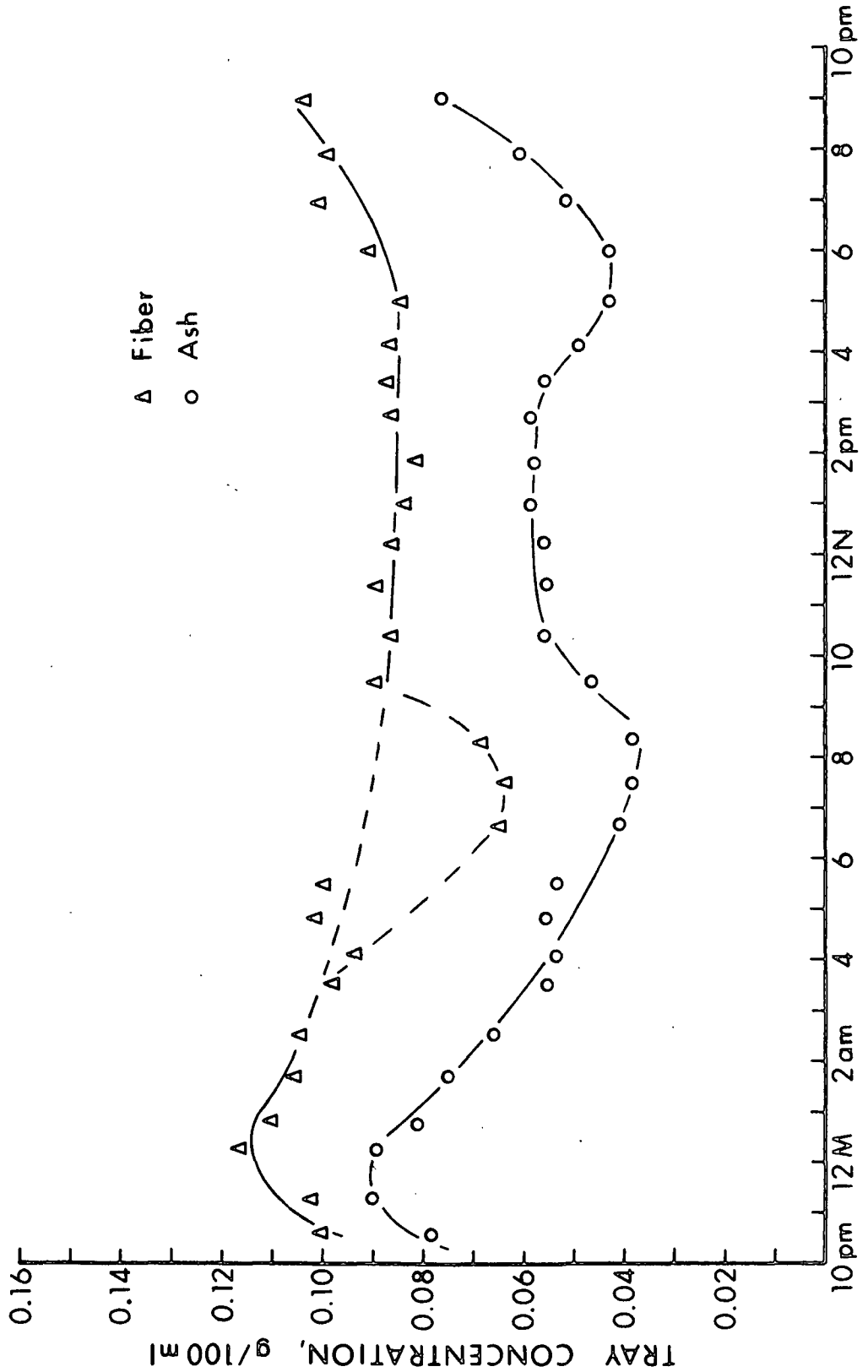

Figure 6. Variation in Tray Water Fiber and Ash During Trial

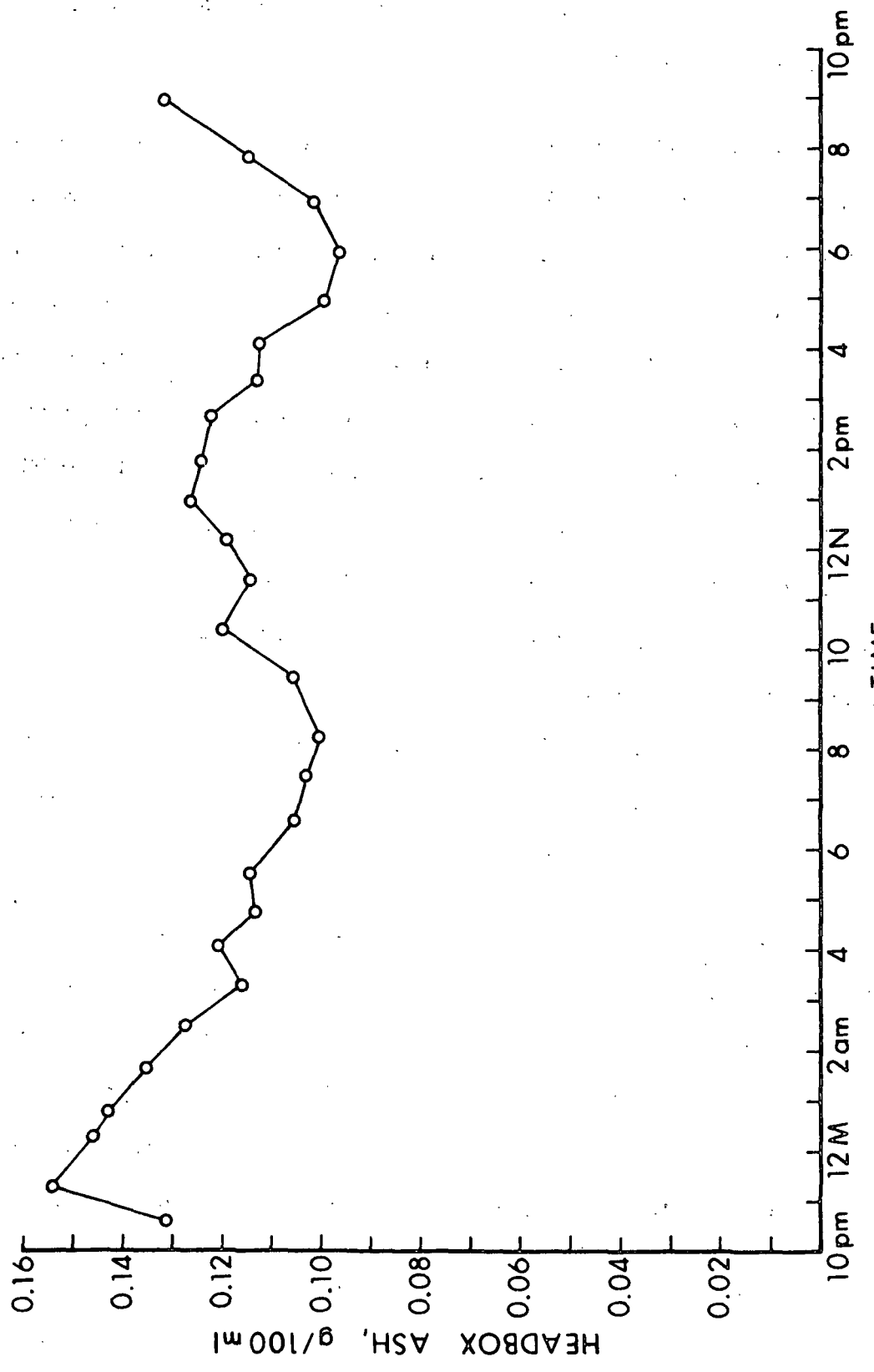

Figure 7. Variation in Headbox Ash During Trial

Fig. 8. The reduction in ash here is important because this stream is sewered and represents a loss of raw material.

A direct measure of the quality of wet end operation is the first pass retention. This was approximated by taking the ratio of the amount of a component in the sheet to that in the headbox both based on a constant weight of fiber. The results for retention of ash and of TiO_2 are shown in Fig. 9. The similarity between the values for the ash and for TiO_2 at a given time imply that both the silica and the TiO_2 react similarly to the effects of the starch, the enzyme treatment and the retention aid. First pass retention rises gradually from a value of 35-40% before enzyme treatment to about 65% during treatment. Reduction of the retention aid dosage just before 9:30 caused an immediate drop of about 5% in retention followed by a recovery of a few percent with time. It appears that there is a slight net loss in retention by decreasing the retention aid dosage, but the overall improvement compared with the base-line portion of the run would still permit the savings in the polymer. Toward the end of the trial, first pass retention falls off again as untreated starch reenters the wet end.

First pass retention of fiber (from a comparison of the amounts in the headbox and the tray water) also shows a slight improvement upon enzyme treatment (Table IX). Values before treatment average 84-86%, during treatment rise to 87-89%, and following cessation of treatment decrease slightly. These improvements in retention of fiber and ash result as previously noted in lower concentrations in the tray water. This in turn should lead to improved operation of the saveall.

The turbidity of the saveall clear leg was perhaps the most dramatic and sensitive measure of the effect of the enzyme treatment. The results are plotted in Fig. 10 for the course of the trial. Initially there is an increase

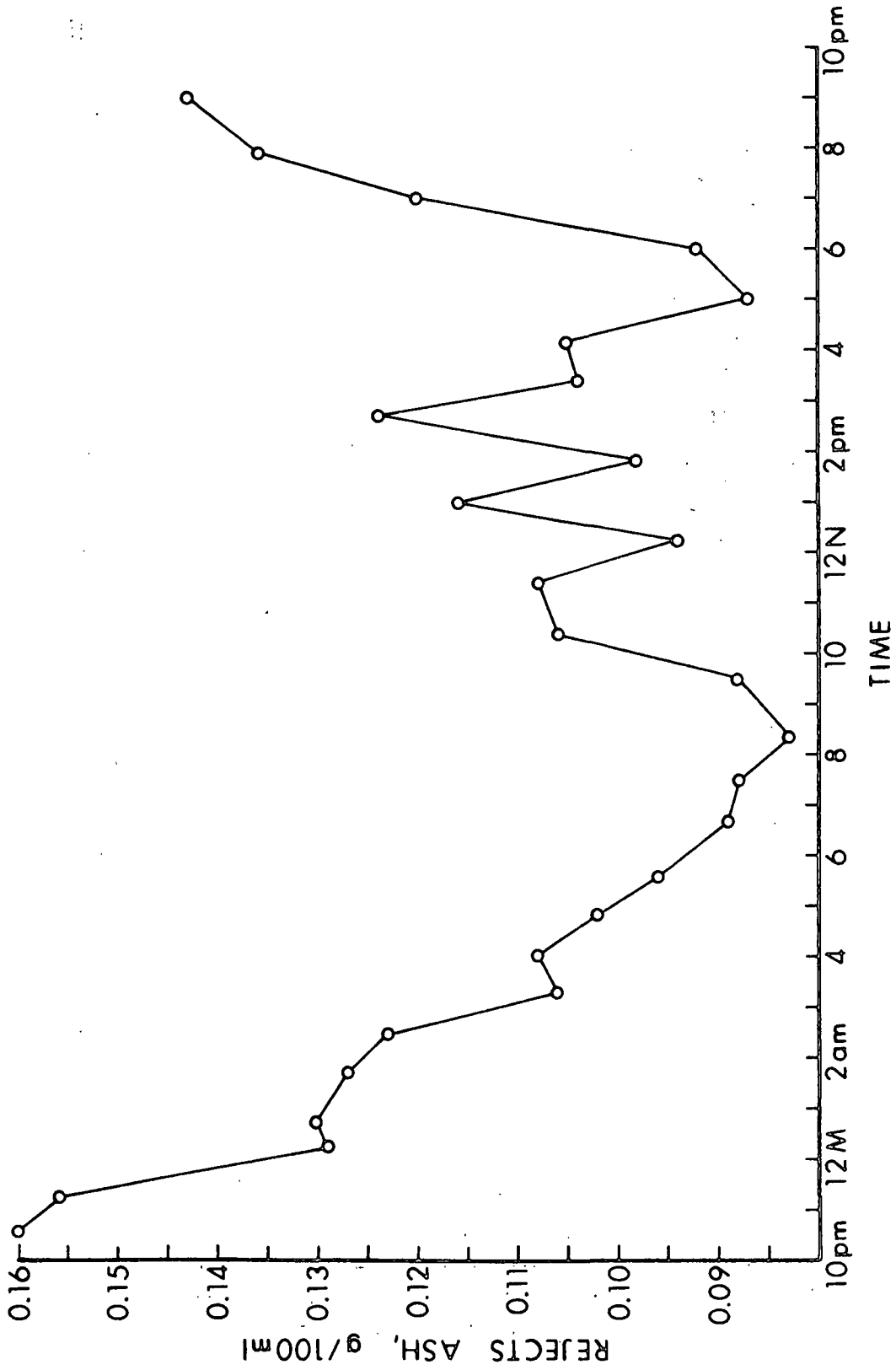

Figure 8. Variation in Ash Content of the Rejects from the Tertiary Cleaners

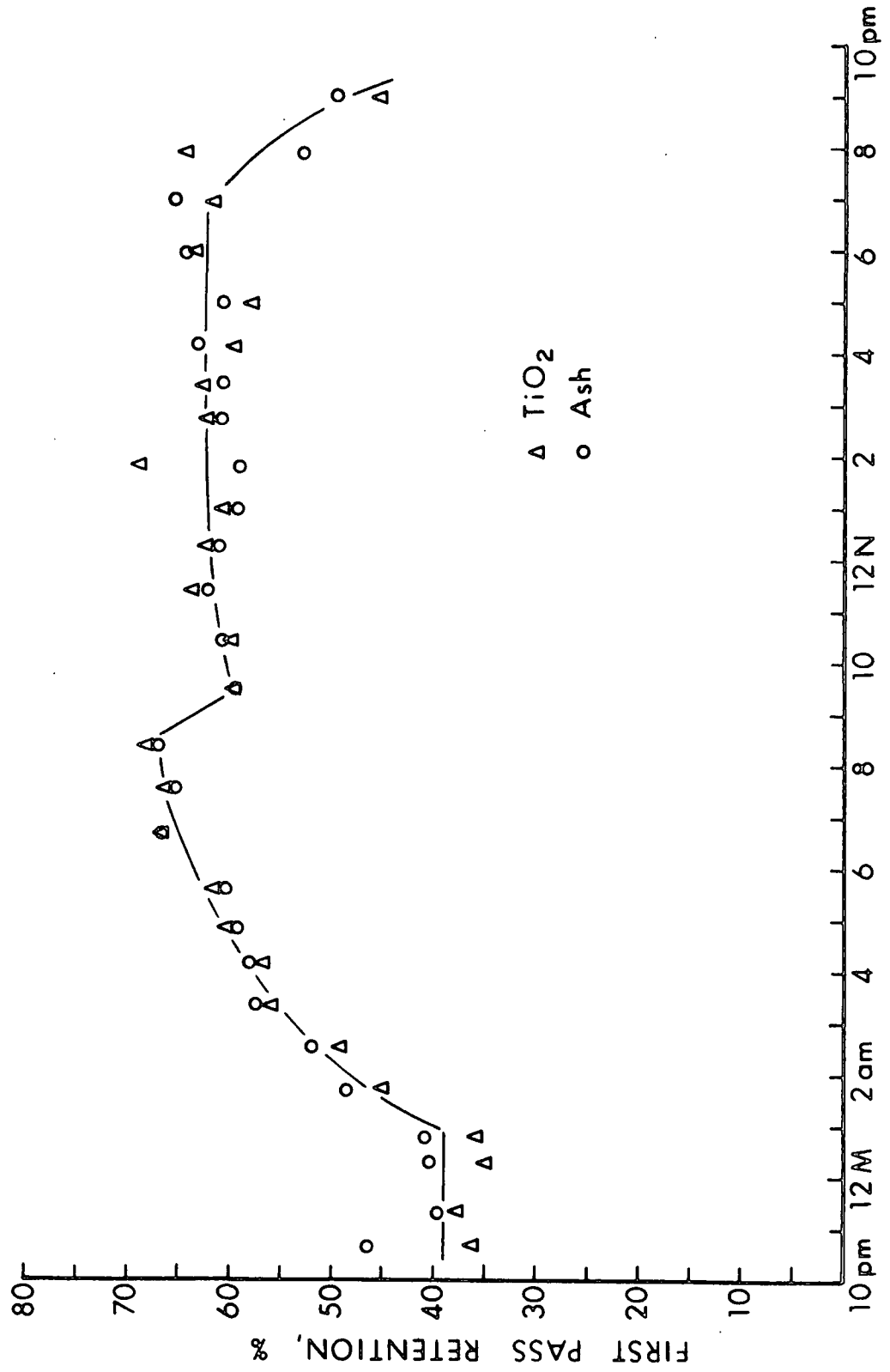

Figure 9. Variation in First Pass Retention of Total Ash and TiO_2 During Trial

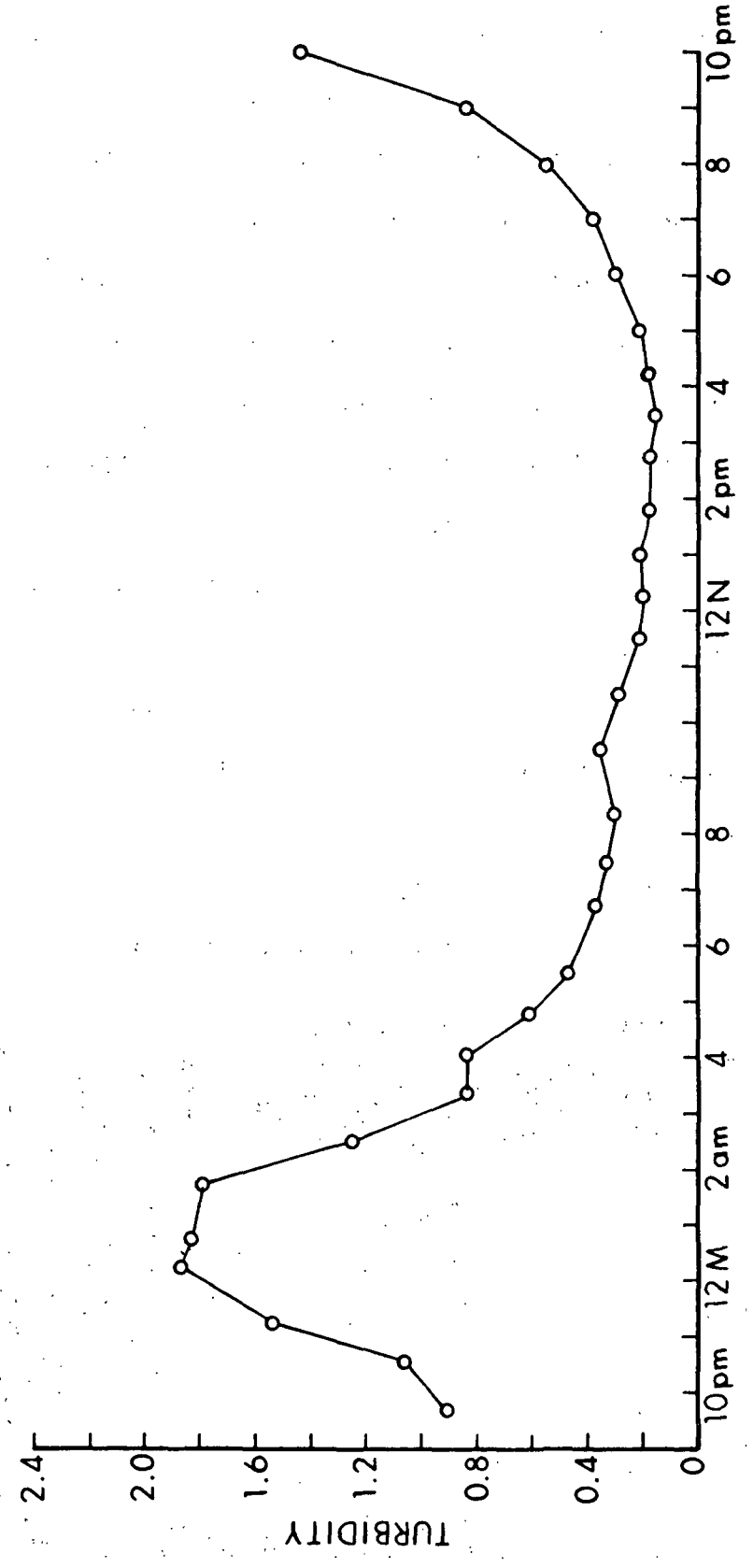

Figure 10. Variation in Turbidity of the Saveall Clear Leg During Trial

in turbidity that reflects the change in grade of paper which was made about 9:30 p.m. (Similar variations during this period can also be noted in Fig. 6-9.) The base-line value of turbidity is 1.8. Introduction of enzyme-treated broke to the stock causes an immediate and drastic decrease in the turbidity. This is because the protective colloid effect of the starch on the filler in both the white water and the sweetener stock (machine chest stock) was decreased. A slight perturbation in the overall decrease was caused by the reduction in retention at dosage at 9:30 a.m. This is followed by a further improvement in the quality of the clear leg until untreated broke again becomes a substantial portion of the stock. Thereupon a rise toward the initial base-line turbidity occurs. A photograph (Fig. 11) of samples taken during the base line (12:45 a.m.) and during treatment (2:45 p.m.) gives a subjective indication of the magnitude of the corresponding change in turbidities. A quantitative measure of the improvement can be made using the data in Table VII. By 8:20 a.m., suspended solids in the clear leg had decreased by 86% and TiO_2 by 87%. Obviously, the saveall is operating in a much more efficient manner during the period of enzyme treatment.

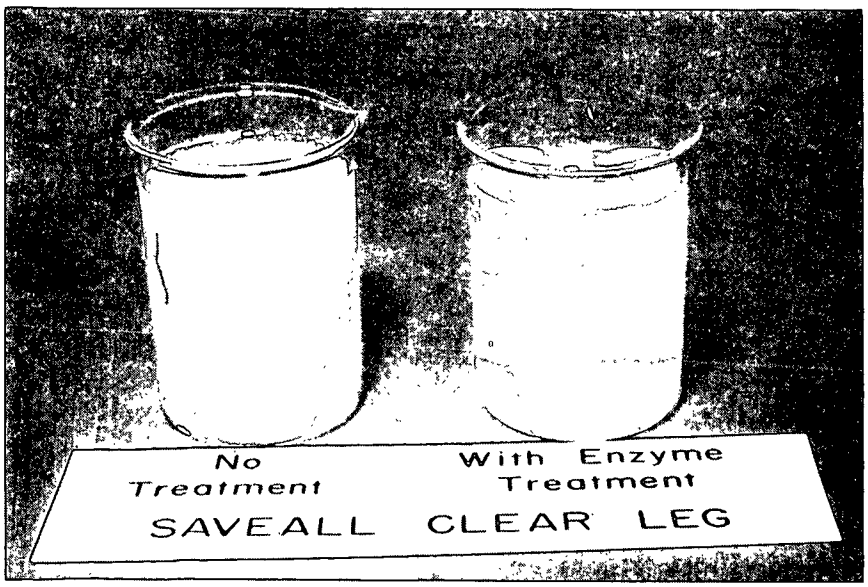

Figure 11. Samples of the Saveall Clear Leg Taken Before Treatment (12:45 a.m.) and During Treatment (2:45 p.m.)

It is important that the enzyme treatment not cause deleterious effects on paper properties. Throughout the trial opacity, brightness, burst strength (Mullen), fold, and tear strength remained within or above specifications. No trends with treatment sequence could be discerned. The enzyme treatment of broke appears to be an effective method for coping with starch in the wet end.

ECONOMIC ANALYSIS

In addition to the demonstration of improved wet end operation, favorable economics must be shown before the enzyme treatment can be considered for implementation in a mill. Although costs or benefits for all factors involved could not be determined with certainty, it is believed that good estimations have been made for the major contributors. The calculable factors can be broken into two categories: raw materials and waste water treatment costs. The raw materials considered here are TiO_2, enzyme, and retention aid. The particular mill where the trial was carried out sends its sewered water to a municipal waste water treatment plant. The mill is charged for volume of effluent, for amount of BOD, and for amount of suspended solids. Thus direct costs for changes in these levels can be determined.

For the analysis the operation of the system at two times, 12:45 a.m. and 8:20 a.m., was compared. The earlier time represents operation during the base-line portion of the trial before enzyme treatment was begun. The later time was after several hours of treatment. The saveall system had not reached its maximum operating efficiency at this time as may be judged by the turbidities in Fig. 10. Rather, the time used was chosen so that measurable amounts of material would be present in the saveall clear leg.

The breakdown of the various factors on the basis of one ton of production is presented in Table X. Only the change due to the treatment is shown.

The cost of the enzyme is seen to be relatively minor. It is based on a furnish containing 30% broke using a treatment level of 2% enzyme on the estimated amount of starch in the broke.

TABLE X

ECONOMICS OF THE ENZYME TREATMENT

(Per ton of paper produced)

	Costs	Savings
Enzyme	$0.34	
Increased sewer costs (BOD)	0.67	
Reduced sewer costs (suspended solids)		$0.24
Reduced retention aid		0.20
TiO_2 saved		1.37
Totals	$1.01	$1.81
Net Savings		$0.80

The BOD costs are calculated from the increase given in Fig. 4, the known daily production (tons paper), and an estimate of the flow to the sewer from the saveall clear leg overflow. (Unfortunately, as mentioned in the RESULTS section, no BOD values for the second trial were obtained.) It is assumed that the change in BOD level is similar for the saveall clear leg and the rejects from the tertiary cleaners. The increase in BOD (Fig. 4) may well be an overestimate for the second mill trial. Because of the much lower enzyme dosage in the second trial, the degradation of the starch is probably not as complete. This is borne out by the finite values of starch in the stuffbox during the period of treatment. The lower turbidity of the saveall clear leg during the first trial also indicates the greater degradation then. Supporting evidence that the actual increase in BOD was not as large as that shown in Fig. 4 comes from the value for the BOD for the entire mill on the day of the trial. This value, on which the actual charge to the mill is calculated, was approximately

equal to that of the preceding day. For the lack of a better figure, however, the cost listed in Table X will be retained.

Part of the increased sewer costs for BOD are offset by lower costs for suspended solids in the effluent. These are calculated from the results in Table VII, the daily tonnage, and the saveall clear leg overflow volume. The savings in TiO_2 is also calculated from these data. It is, by far, the largest item to be considered and is a major incentive for implementation of the enzyme treatment. Finally, the savings in retention aid is that resulting from a decrease in its dosage from 0.33 to 0.07 lb/ton while maintaining opacity and brightness.

Other (minor) savings not included in Table X because the necessary data were lacking include: savings in raw materials costs for silica and fiber due to more efficient operation of the saveall (Table VII) and savings in raw materials and suspended solids sewer costs due to decreased ash (TiO_2 and silica) in the rejects stream from the tertiary cleaners (Fig. 8).

One possibly important additional cost that was not included in Table X (for want of the necessary data) concerns the degraded starch leading to the increase in BOD. In addition to the cost for BOD the loss in the raw material must be accounted for. A detailed material balance on this component would be necessary to determine the magnitude of the loss.

The net savings in Table X of $0.80/ton due to the enzyme treatment is, perhaps, not a large sum. There are other benefits on which it is hard to place quantitative values, but which nevertheless represent true savings. Among these are:

— Stable operation of the saveall. With the enzyme treatment in operation, the system will not be subject to upsets brought about by fluctuations either in the amount of starch in the broke or in the amount of broke in the stock. A reliable source of clarified water is the result.

— Uniform opacity throughout a run. With a relatively constant, low amount of starch in the wet end, the first pass retention will not be subject to the fluctuations of starch in the broke; ash in the sheet will be constant.

— Better quality of the saveall clear leg. This results in less clogging of shower heads by particulates. It is probable that this improved stream could be used for other more demanding applications in the mill, thereby increasing closure. This would lead to a smaller flow to the sewer with attendant reduction in costs.

— Fewer fines in the headbox. Improved first pass retention results in fewer fines (filler and pulp) in the headbox. This in turn provides better drainage, reduced plugging and longer life of the felts, and less two-sidedness of the sheet.

It is apparent that use of the enzyme treatment of the broke can lead to smoother operation with overall savings.

APPLICATIONS TO OTHER MILL SYSTEMS

This report has shown the utility of the enzyme treatment when the only starch in the system is that applied at the size press. Many mills, however, may also add cationic starch at the wet end as a beater adhesive or as a retention aid. Carry over of active enzyme from the broke chest to the wet end could lead to degradation of the cationic starch (10) and loss of its effectiveness. There are several possible approaches to this problem.

If the cationic starch is an effective retention aid for the filler in spite of the presence of other starch from surface sizing, it may only be necessary to treat the stream to the primary clarifier to aid flocculation there. The enzyme could be added to the sewer sump (10) or other point where the pH and holding time could be controlled. Wu (11) has shown that a time as short as ten minutes may be sufficient to effectively degrade the starch. This treatment point may also be useful to those mills where the loss of starch as a raw material by treatment in the broke hydrapulper may be economically unattractive. In this case the improvement is not in the wet end but in the operating efficiency of the primary clarifier.

A second method might be to treat the surface sized broke in the hydrapulper (as in this report). The enzyme would then need to be denatured before the repulped broke was mixed with the virgin pulp and cationic starch. Several methods are available to inactivate enzyme. These include heat, small amounts of heavy metal ions, and certain chemicals. The addition of trace amounts of copper or the use of some slimicides or bleaching chemicals would appear to be feasible. The particular method and amount of additive would need to be determined for the particular enzyme used. It is possible that mere inhibition of the

enzyme in the wet end by adjustment of pH would be sufficient to allow the joint use of enzyme in the hydrapulper and cationic starch in the wet end. For example, on the basis of Fig. 1 and 2, maintaining a pH less than 5 in the wet end would completely inhibit the α-amylase used in this study.

A third, and perhaps more drastic, alternative would be to replace the wet end cationic starch by one of the natural gums or by a synthetic polymer. The replacement may be more expensive than the cationic starch but the benefits of improved retention, saveall operation, and primary clarifier operation may more than offset the extra cost.

Another type of mill system is one where the starch-containing material is coated broke. Exploratory studies (16) using the enzyme treatment on samples of coated broke from a mill were not successful. Although the starch was available to harm TiO_2 retention when treated broke was mixed with virgin pulp and filler, it apparently was not accessible to the enzyme. Alternatively, some unknown factor may have inhibited the enzyme catalysis. Further work with such systems might provide effective methods for treating coated broke, also.

The enzyme discussed in this report is alpha-amylase which attacks the internal α-1,4 glucan links in starch at random. Its optimum pH is reported to be 6.9 (17) although our studies gave maximum improvement in retention at pH 7.5. In previous work (10,11) another enzyme, beta-amylase, was used. It attacks the starch molecule from the nonreducing ends of the chain removing successive maltose units by hydrolysis of the α-1,4 glucan linkages. Beta-amylase has optimum activity at pH 4-5 (11,17) although Schwonke and Davis report highest activity at neutral or near neutral pH. From the results of previous studies (10,11) and those presented here it would appear that either enzyme could be effectively used

to decrease the protective colloid forming ability of starch. Because of the different optimum pH levels for the two, a particular mill might find one more suited to its system than the other.

In review, the factors that need to be considered or determined before a particular mill can effectively use the enzyme treatment system are:

1. Type of enzyme: alpha-amylase or beta-amylase
2. Minimum reaction time required for effective treatment
3. Minimum enzyme dosage consistent with effective treatment
4. Optimum pH
5. Effect of range of temperatures to be encountered in the hydrapulper
6. Method of inactivating the enzyme before addition to main pulper (if necessary)
7. Effect of bleaching agents which are added to the hydrapulper when using colored broke
8. Check for denaturation of the enzyme in the driers before the size press
9. Determine whether the overall economics of the treatment are favorable, including the cost of loss of the degraded starch
10. Determine whether the additional BOD load on the secondary waste treatment system can be accommodated.

The possibilities for successful use of the enzyme treatment in many mills to improve wet end and primary clarifier operation are good.

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